

# UK Patent Application GB 2 151 662A

(43) Application published 24 Jul 1985

(21) Application No 8427276	(51) INT CL <sup>4</sup> C23C 16/44 // C23C 16/18
(22) Date of filing 29 Oct 1984	
(30) Priority data	
(31) 3339625      (32) 2 Nov 1983      (33) DE	(56) Documents cited None
(71) Applicant N. V. Philips' Gloeilampenfabrieken, (Netherlands), Groenewoudseweg 1, 5621 BA Eindhoven, The Netherlands	(58) Field of search C7F C1A B1H
(72) Inventors Georg Gartner, Helmut Grosche	
(74) Agent and/or address for service R. J. Boxall, Mullard House, Torrington Place, London, WC1E 7HD	

## (54) Device for enriching a carrier gas with the vapour of a slightly volatile material for chemical vapour deposition method

(57) The device comprises a container (1) having a heatable inner space (3) for receiving a fine-particle, sparingly volatile material or mixture of materials, a gas inlet (4) and a gas outlet (5), and the container (1) comprises a removable tightly-fitting metal member (2), having a groove (3) preferably wound in the form of a spiral or in a zigzag-like or meander-like manner provided in at least one outerwall of the metal member, and said outer wall being in contact with an inner wall, preferably the bottom, of the container, in such manner that the groove forms the said inner space. The device has a long flow path and can easily be cleaned.

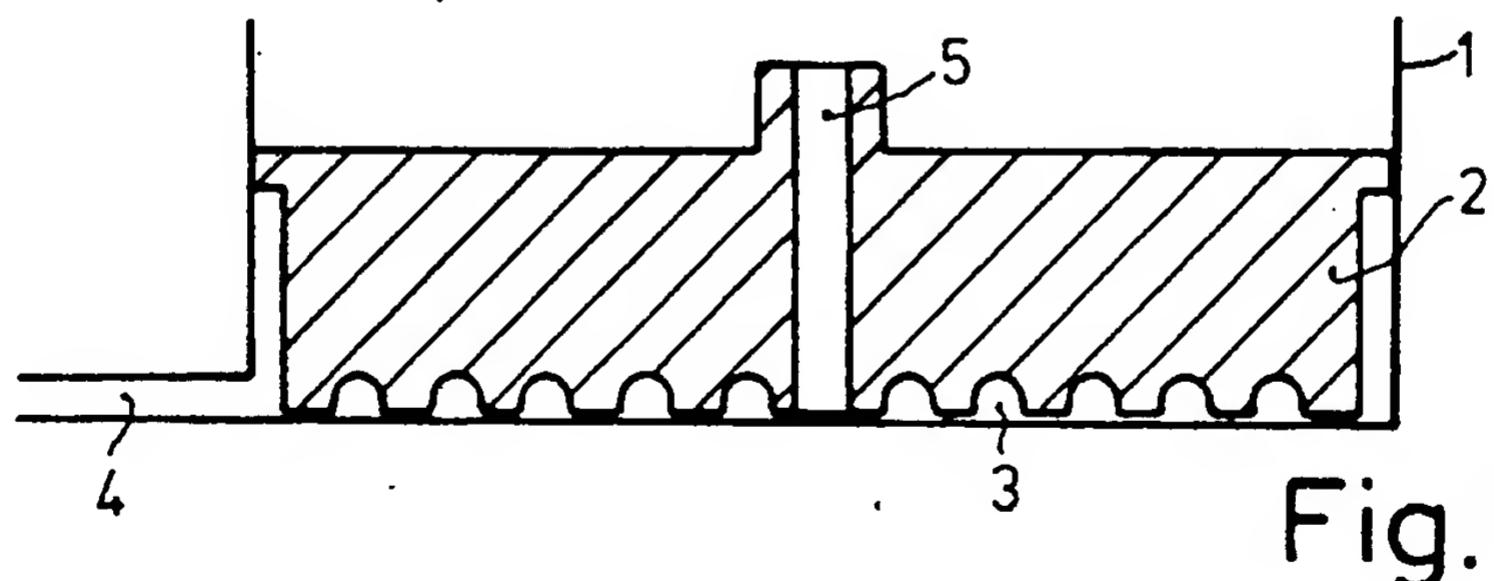


Fig.1

GB 2 151 662 A

1/2

2151652

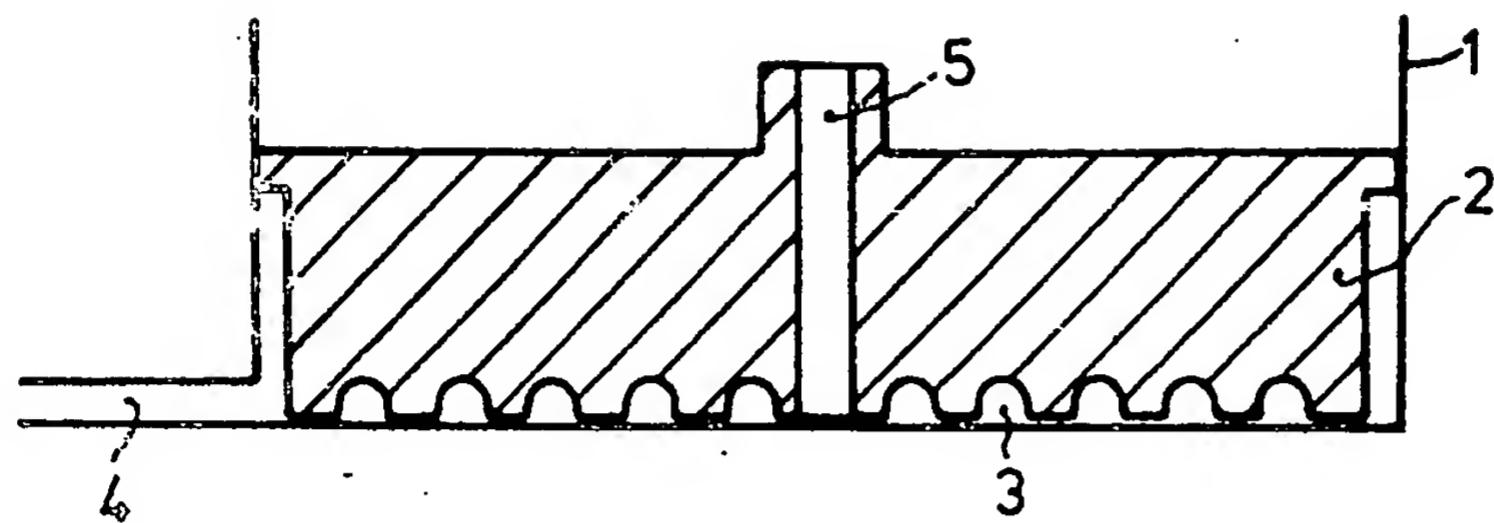


Fig.1

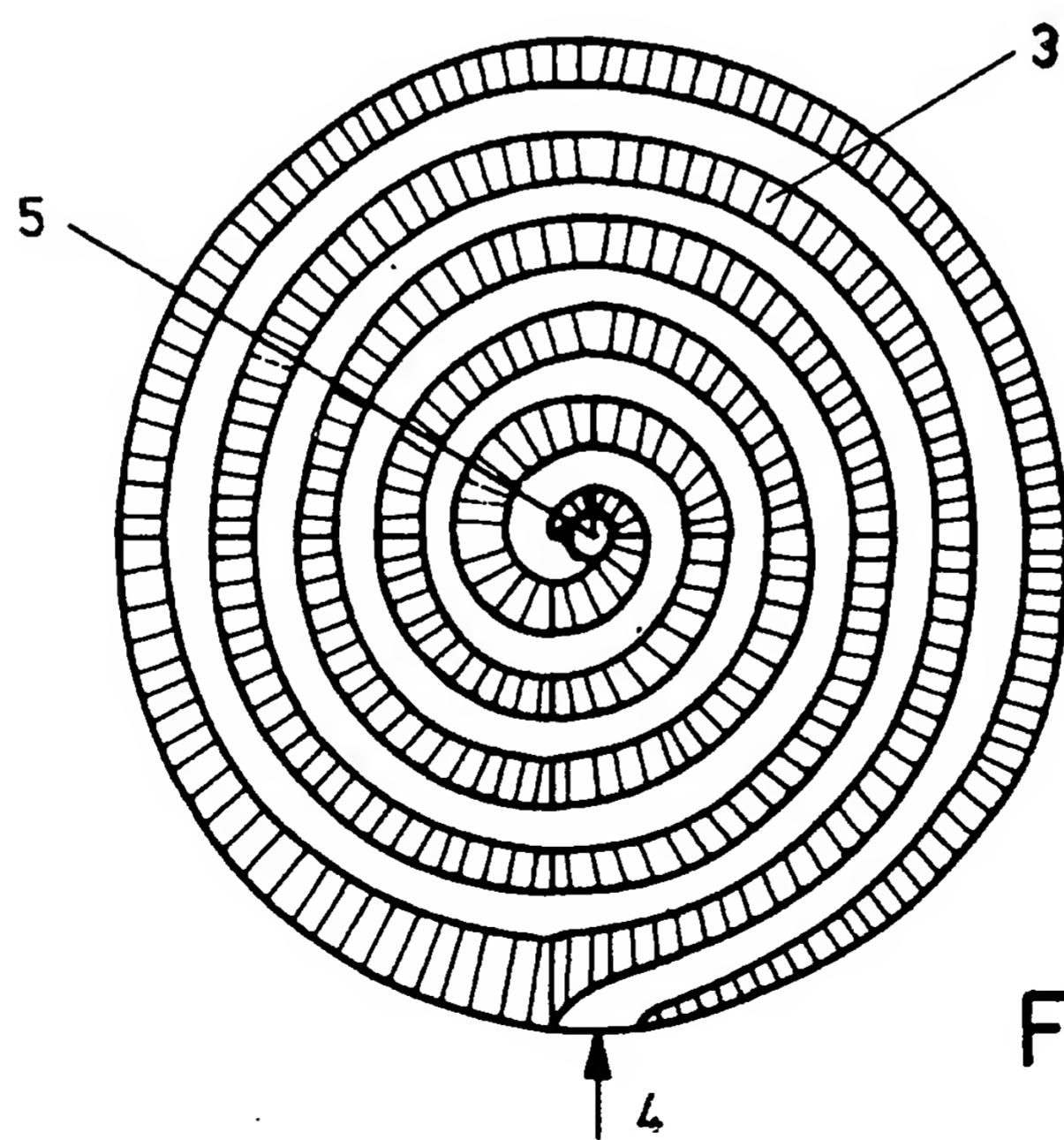


Fig.2

2151632

2/2

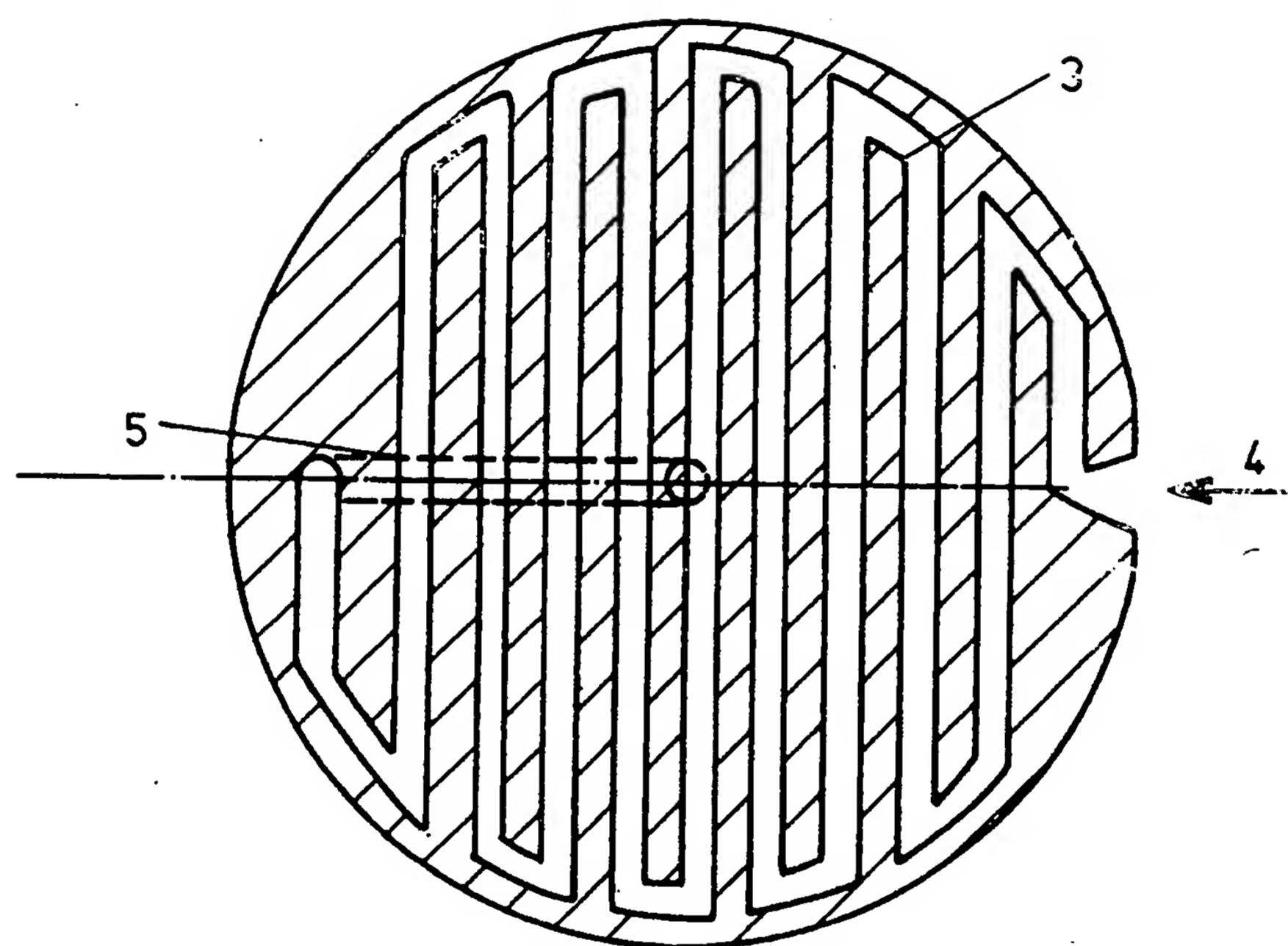


Fig.3

**SPECIFICATION****Device for Enriching a Carrier Gas with the Vapour of a Sparingly Volatile Material**

5 The invention relates to a device for enriching a carrier gas or carrier gas mixture with the vapour or vapours of a sparingly volatile material or mixture of materials present in the form of solid particles, comprising a container having a heatable inner space for receiving the material or mixture of

10 materials which is provided with an inlet for the carrier gas and an outlet for the enriched carrier gas, the pipes opening into the inner space in such manner that the carrier gas during operation of the device flows through the material or the mixture of

15 materials.

Such a device is known from DE-OS 31 36 895. The known device consists of an evaporation vessel with cover. Inside the evaporation vessel a sieve is present on which during operation of the device a

20 starting material is present in the form of a powder. A heating element is provided below the sieve or in the proximity thereof in the evaporation vessel. From a carrier gas storage container an inlet leads to the evaporation vessel, the inlet opening below the

25 sieve. From the inner space of the evaporation vessel above the sieve a vapour outlet leads to a reactor in which a reactive deposition from the gaseous phase takes place in which hence a CVD-method is carried out.

30 The investigations which have led to the present invention relates to the enrichment of carrier gases with gases for the reactive deposition in particular of rare earth metals (III-B-metal) and rare earth metal compounds (III-B-compounds), respectively, and of

35 thorium and thorium compounds, from the gaseous phase. Since the starting compounds in question for the CVD-method as a rule are present as metalorganic compounds in powder form at room temperature—only these are slightly volatile already

40 with slight heating—the starting compound is transported by a carrier gas to a substrate surface on which layers are to be deposited. The carrier gas, preferably a noble gas, in particular argon, flows through a saturator which is filled with the starting

45 compound in powder form and is heated to a suitable temperature.

The device known from DE-OS 31 36 895 suffers from the disadvantage of having only a short flow path of the gas through the gas-forming material.

50 The yield of reaction gas for the CVD-method and its concentration in the gasflow, respectively, are correspondingly low.

It is the object of the invention to provide a device of the kind mentioned in the opening paragraph, in

55 particular a saturator, which has a long flow path. According to the invention this object is achieved in that the container comprises a removable tightly fitting metal member, that at least one groove is provided in at least one outer wall of the metal member, and that said outer wall is in contact with an inner wall of the container in such manner that the groove forms the said inner space.

In order to achieve a flow path which is as long as possible, the groove must be as long as possible.

65 For this purpose it is advantageous for the groove to be wound in the form of a spiral or in a zigzag-like or meander-like manner.

The outer wall of the metal member in which the groove is provided is preferably in contact with the bottom of the vessel. From this it follows that the groove is preferably provided in the lower side of the metal member. However, it is also possible for the groove to be provided in the side walls of the metal member.

70 In order to avoid particles of the material or mixture of materials being dragged along by the carrier gas it is advantageous to provide a gas-permeable member between the gas outlet and the inner space.

75 The device according to the invention has the advantage that it can be filled in a simple manner with the fine-particle vapour-forming material or mixture of materials, for example a powder. For example, for filling a saturator according to the

80 invention the groove formed in the lower side of a copper block is pressed down to the bottom of a tray or pan of V2A noble steel filled just sufficiently with the powder. During operation, the carrier gas flows through the groove thus filled.

85 A helical construction of the groove has the additional advantage that by means of a rotary movement in the spiral outer direction a dense filling of the grooves with the powder is achieved and at the same time the bottom contact of the

90 contacting surfaces becomes really good.

A further advantage of the device according to the invention is that its parts, after removing the metal member, can easily be cleaned.

95 A few embodiments of the invention are shown in a drawing and will be described in greater detail hereinafter. In the drawing:

100 Fig. 1 is a sectional view of a saturator, Fig. 2 shows a removable metal member (metal insert) with spiral-like groove, and

105 Fig. 3 shows a removable metal member (metal insert) with meander-like groove.

The sequence in time of the operation of the saturator shown in Figure 1 is as follows.

First, fine gas-forming powder is filled in a

110 container 1 of noble steel. A tightly fitting copper block 2 having a spiral groove 3 in its lower side is then pressed firmly on the powder, namely by means of a rotary movement against the subsequent direction of flow, and is fitted to the

115 carrier gas inlet 4 and locked by a pin (not shown). The gas outlet 5 is in the centre of the copper block and comprises a mesh grid and  $Al_2O_3$  wool provided in front of it. This combined sieve is to prevent emanation of the powder.

120 A further copper insert, for example a hollow cylinder with sealing and outlet aperture (not shown) may be provided above the copper block 2 and be clamped on the saturator block with fixed pressure by means of a bayonet. The space between

125 the copper insert and the saturator block then forms a mixing chamber for further CVD starting gases. Via its outlet nozzle the substrate to be coated may then be provided in a reactor (not shown).

Fig. 2 shows a metal member 2 having a spiral-like

groove 3 and Fig. 3 shows a metal member 2 having a meander-like groove 3 in which the carrier gas inlet is referenced 4 and the gas outlet is referenced 5.

5 The outer walls of the saturator and reactor consists of V2A noble steel and are constructed so as to be high vacuum-tight. They are present in a furnace having a separate heating for the saturator and for the reactor and the mixing chamber. During 10 operation the latter are at a slightly higher temperature than the saturator so as to avoid deposition on the wall of the III B starting compound. After a series of coatings, cleaning of the saturator and a renewed filling with the starting 15 compound as a rule is necessary since many of the powdered metalorganic starting compounds used start to dissociate already near the melting point, but exactly there also have the highest vapour pressure realisable in the long run. Moreover, a 20 successive decomposition by contact with the aggressive compounds (for example  $WF_6$  and HF) formed during the CVD method may be caused.

For cleaning purposes the whole arrangement can be taken apart with few manipulations and be 25 cleaned by means of a brush in dilute solutions of detergents followed by rinsing with water and ethanol.

In using the saturator thorium acetyl acetonate (Th(AA)<sub>4</sub>) and thorium trifluoroacetyl acetonate 30 (Th(3FAA)<sub>4</sub>) were used as powdered starting compounds and argon was used as a carrier gas. The saturator temperature for the filling with Th(AA)<sub>4</sub> was  $160^\circ\text{C} \pm 5^\circ\text{C}$  and for the Th(3FAA)<sub>4</sub> filling it was 100 to  $120^\circ\text{C}$ . The reactor temperature was 20°. 35 above the saturation temperature. As deposition rates for the layers containing thorium approximately 0.1 to 0.4  $\mu\text{m}/\text{min}$  were reached which strongly reduced for Th(AA)<sub>4</sub> in the each time

third coating and for Th(3FAA)<sub>4</sub> could be realised for 40 approximately 6 coatings, the duration of a coating being at most 4 hours.

#### CLAIMS

1. A device for enriching a carrier gas or mixture of carrier gases with the vapour or vapours of a sparingly volatile material or mixture of materials 45 present in the form of solid particles, comprising a container having a heatable inner space for receiving the material or mixture of materials which is provided with an inlet for the carrier gas and an outlet for the enriched carrier gas, the pipes opening into the inner space in such manner that the carrier gas during operation of the device flows through the material or the mixture of materials, characterized in that the container comprises a removable tightly 50 fitting metal member, that at least one groove is provided in at least one outer wall of the metal member, and that said outer wall is in contact with an inner wall of the container in such manner that the groove forms the said inner space.
2. A device as claimed in Claim 1, characterized in that the groove is wound in the form of a spiral or in a zigzag-like or meander-like manner.
3. A device as claimed in Claim 1 or 2, characterized in that the outer wall of the metal 55 member in which the groove is provided is in contact with the bottom of the vessel.
4. A device as claimed in Claim 1, 2 or 3, characterized in that a gas-permeable member is provided between the gas outlet and the inner wall.
5. A device for enriching a carrier gas or mixture of carrier gases with the vapour or vapours of a sparingly volatile material or mixture of materials 70 present in the device in the form of solid particles, substantially as herein described with reference to Figures 1 and 2 or to Figure 3 of the drawings.